

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 237 258 B1

(12)

EUROPEAN PATENT SPECIFICATION(43) Date of publication of patent specification: 16.02.94 (51) Int. Cl.⁵: G09F 3/04, H01B 7/36

(21) Application number: 87301865.9

(22) Date of filing: 04.03.87

(54) **Marker assembly.**(30) Priority: 04.03.86 GB 8605306
18.09.86 GB 8622492(43) Date of publication of application:
16.09.87 Bulletin 87/38(45) Publication of the grant of the patent:
16.02.94 Bulletin 94/07(94) Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE(56) References cited:
EP-A- 0 118 687
EP-A- 0 158 925
GB-A- 2 117 270
US-A- 3 344 528
US-A- 4 349 404(73) Proprietor: RAYCHEM LIMITED
Rolls House
7, Rolls Buildings
Fetter Lane
London, EC4 1NL(GB)(72) Inventor: Neaves, Bryan David
51 Wheeler Avenue
Swindon Wiltshire(GB)
Inventor: Hill, Frederick William Leslie
44 Kingsmead
Lechlade Gloucestershire(GB)
Inventor: Cross, Malcolm Gordon
1 The Lane
Hempton
Deddington Oxfordshire, OX5 4QT(GB)(74) Representative: Dlugosz, Anthony Charles et al
Raychem Limited
Intellectual Property Law Department
Faraday Road
Dorcan
Swindon, Wiltshire (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to marker assemblies, for example panel markers or marker sleeves for marking wires, cables and the like.

5 There is often a need for identifying components in complex wiring and cable assemblies, and a number of methods have been proposed. For example it has been proposed to produce heat-recoverable markers, either in the form of sleeves or tape, which can be positioned on the object to be marked and recovered so that they are held tightly on the object. Examples of such systems are described in U.S. Patents Nos. 3,894,731, 4,032,010 and 4,206,909 and in British Patent Specifications Nos. 2,059,913A and 10 2,082,110A. One system which comprises a support later having a porous surface layer comprising a particulate material and a binder is described in EP-A-158,925.

One disadvantage of all such systems is that when the object that is marked is subjected to mechanical abuse, it is possible for the indicia on the marker to be erased. This problem is overcome to some extent with the heat-recoverable systems mentioned above by subjecting the printed marker sleeves to a so-called 15 "permatizing" operation in which the sleeves are exposed to an infrared radiation source for a short period of time. This procedure, however cannot prevent erasure of indicia when the object is subjected to severe mechanical abuse, for example abrasion of the wire or cable when being pulled through a bulkhead, in which the surface of the marker may be completely worn away. In addition indicia may be erased when the assembly is exposed to solvents and other fluids.

20 In addition to the marking of wires and cables it is often necessary to provide other objects such as walls, doors, machinery and the like of buildings, vehicles, air and sea craft with identification or other information. This has usually been achieved by means of plastics or metal sheets on which characters have been formed by screen printing. Such markers, however, suffer from very poor solvent resistance. Alternatively, objects may be marked by means of rigid plastics laminates that are engraved with the 25 necessary information and are then screwed in place. Although such laminate markers are usually highly resistant to solvents and mechanical abuse, they suffer from a number of disadvantages: They need to be engraved which increases their cost and reduces their ease of use since the customer usually does not have the necessary equipment for forming the indicia; they are relatively heavy, which is a serious disadvantage when used in aircraft; and they are not capable of being secured to curved surfaces such as 30 pipes and the like.

The present invention provides a marker assembly, which comprises a support layer having a surface that is provided with a porous coating of a latent curable material that is capable of receiving printed indicia and that can be subsequently be cured to render the indicia substantially indelible, the porous coating being 35 in particulate and/or filamentary form. The assembly is preferably arranged to be secured to an object or surface with the cured coating exposed.

As stated above, the coating material is formed from a latent curable material, that is to say, that the choice of material enables the assembly to be made, distributed and marked before the coating has cured sufficiently to prevent absorption of the ink. Preferably the assembly can be stored for at least 3 months and especially at least 6 months at ambient temperatures before printing.

40 Whether or not indicia are substantially indelible will depend amongst other things on the ink that is used to form the indicia, and, in particular, on whether it is absorbed or rejected by the curable marker coating material in its uncured state, only those inks that are absorbed by the marker coating being considered appropriate for use with that marker. Indicia that are formed on the coating are considered herein to have been rendered substantially indelible if they can withstand the solvent test specified in 45 Example 1 below with no significant loss of legibility of the indicia in respect of the solvents listed other than any solvents that swell the coating material.

In many instances, however, there will be no significant loss of legibility of the indicia even with solvents that do swell the coating material.

50 The markers according to the invention have the advantage that they are in general resistant to a broader range of solvents than equivalent non-curable polymeric markers, by virtue of the curing of the coating material. In addition, the curing of the coating material can often improve the thermal stability of the marker.

In one preferred embodiment the marker assembly according to the invention may be used as a panel 55 marker for providing information on flat surfaces such as doors, walls, bulkheads and the like and also on curves surfaces such as pipes, cyclinders and the like. In this embodiment the support layer is in the form of a flat sheet, preferably comprising a polymeric material. The sheet may be arranged to be secured to the surface by any appropriate means, for example screws or bolts but will usually be secured by means of a layer of adhesive on the surface of the support layer opposite the porous coating. Preferred adhesives

include hot-melt adhesives, cyanoacrylate adhesives, contact adhesives or pressure-sensitive adhesives, e.g. acrylic adhesives. Examples of preferred hot-melt adhesives include those based on olefin homo or copolymers such as ethylene-vinyl acetate or ethylene-ethyl acrylate copolymers, or polyamide hot-melt adhesives, for example those described in U.S. Patent No. 4,018,733 to Lopez et al the disclosure of which is incorporated herein by reference.

The support layer may be formed from any of a number of materials depending on the degree of mechanical abuse or exposure to chemicals the marker is likely to experience. The support layer should also be able to withstand any heat to which it is exposed when the porous coating is cured. Suitable materials for forming the support layer include aluminium, aromatic ether ketones e.g. polyesters especially polyethylene terephthalate for example sold under the trademark "Mylar" or other polyesters e.g. "Hytrel", polyolefins, fluoropolymers such as polyvinylidene fluoride, polyamides such as nylon 6, nylon 6.6, nylon 11 or nylon 12 and other polymers or metals. The material may be modified if desired to provide it with additional properties, for example the material may incorporate halogenated or halogen-free flame retardants, especially halogen free flame retardants such as hydrated alumina or hydrated magnesia. The material may incorporate additional or alternative fillers in order to pigment it, especially to form a white layer, or one surface, preferably the surface opposite the surface carrying the porous coating, may be metallised, in which case the support layer is preferably transparent or translucent. Other fillers include luminescent materials such as those based on doped zinc sulphide or cadmium sulphide or reflective fillers for example glass microspheres or metal flake. The support layer may be treated in order to improve adhesion, for example by corona discharge, acid etching, plasma treatment or flame treatment.

It may be preferred to cross-link the support layer either chemically or by irradiation e.g. by gamma radiation or by high energy electrons in order to improve the layer's resistance to heat. In a typical chemically cross-linked composition there will be about 0.5 to 5 weight per cent of peroxide based on the weight of the polymeric composition. The cross-linking agent may be employed alone or in association with a co-curing agent such as a polyfunctional vinyl or allyl compound, e.g. triallyl cyanurate, triallyl isocyanurate or pentaerythritol tetra methacrylate.

Radiation cross-linking may be effected by exposure to high energy irradiation such as an electron beam or gamma rays. Radiation dosages in the range of 2 to 80 Mrads, preferably 2 to 50 Mrads, e.g. 2 to 20 Mrads and particularly 4 to 15 Mrads are in general appropriate.

For the purpose of promoting cross-linking during irradiation preferably from 0.2 to 5 weight per cent of a prorad such as a polyfunctional vinyl or allyl compound, for example, triallyl cyanurate, triallyl isocyanurate or pentaerythritol tetramethacrylate are incorporated into the composition prior to irradiation.

As stated above, the porous coating is in a particulate and/or filamentary form, for example it may be in the form of a mat of filaments or in the form of a mat that contains particulate material dispersed therein. Preferably, however, the porous coating is substantially entirely in particulate form, in which case the particles preferably have a weight average particle size of not more than 50 micrometres and especially not more than 25 micrometres, the preferred coatings having a particle size less than 10 micrometres. It has been found that coatings having particle sizes substantially greater than 100 micrometres may lead to surfaces that have unacceptable roughness. The use of a particulate and/or filamentary coating not only improves the ink receptivity of the coating, but also enables coatings to be formed that are heat-curable but that also have a high degree of latency. That is to say, coatings may be formed that will readily cure within a relatively short length of time when heated, but can be kept for months or even years at ambient temperatures with substantially no premature curing. Such a high degree of latency may be achieved by processing the reactive components of the coating into separate particles and mixing the particles together to form the coating. Thus, the components will exist separately from each other until they are heated, whereupon they will fuse together and react. However, in other cases the reactive components may be melt blended together before comminution.

The porous coating may, if desired, consist solely of the reactive components although it may include one or more inert components. The inert components may be present with the reactive components in the particles, or may be mixed with the particles as a separate phase or both. For example, the coating may comprise a particulate curable resin such as an epoxy resin, preferably one based on bisphenol A or on epoxy novolak resin, as one component and a particulate curing agent having reactive amine groups or a carboxylic acid, phenolic resin isocyanate or polyester curing agent as the other. The curing agent may itself be polymeric for example it may be a polyamide having free amino groups or a carboxylated polymer such as an acid terpolymer, in which case the particles of the curing agent need not contain any inert component. If the curing agent is not polymeric, for example an organic peroxide or other free radical initiator, it may be desirable for it to be blended with a polymeric material, e.g. a polyester or a reactive or unreactive polyamide before comminution. The curable resin, may instead, comprise a polyamide having

free amine groups which case the curing agent preferably comprises a material having free or blocked isocyanate functional groups, e.g. a cresyl blocked isocyanate. Other curing systems that may be mentioned are unsaturated polyesters or polyurethanes that are cured by a blocked isocyanate curing agent, and polyesters that are cured by a polyepoxide.

5 Polyamides that may be used for forming one of the components are those that are conventionally used as hot-melt adhesives. These polyamides are characterized by the fact that their amide linkages are separated by an average of at least fifteen carbon atoms and have amorphous structures in contrast with the more highly crystalline, fibre forming polyamides such as nylon 6 or nylon 6.6. The polyamides preferably have an amine number of at least 5, the upper limit for the amine number being determined by 10 the fact that as the amine number increases the polyamides become liquid at lower temperatures. Such polyamides have the advantage that they may also be used to improve the flexibility of the cured coating.

Alternatively or in addition the or at least one material having reactive amine groups is one based on a polymer that is the same as or similar to that on which the epoxy resin is based. For example, and preferably, the or at least one material containing reactive amine groups is an adduct of the epoxy resin that 15 is used with a compound containing reactive amine groups, preferably with an aliphatic diamine or triamine and especially with ethylene diamine or ethylene triamine. The use of an epoxy-amine compound adduct as the other reactive component or one of the other reactive components can significantly improve the cure rate of the adhesive in relation to its storage life, thereby permitting the storage life of the adhesive or the cured properties thereof to be improved.

20 Chemical curing accelerators may also be present in the coating, either blended with one of the reactive components or as separate particles. Examples of accelerators include dimethylaminopyridine, tris (dimethylaminomethyl) phenol, tin octoate, imidazole or imidazole derivatives such as salts, substituted imidazoles or metal complexes thereof.

Preferred materials for forming the porous coating are described in British Patent Specification No. 25 2,104,800A and European Patent Application No. 157,478, the disclosures of which are incorporated herein by reference. The coating may be applied onto the support layer for example as a dispersion in a suitable non-solvent optionally containing a binder therein, and dried on the support layer. The binder level should be sufficiently great as to form a coatable film and binder levels of up to 15% and preferably from 2 to 15% based on the weight of the other components are found to be appropriate although in some instances 30 higher levels may be preferred. The material may be applied onto the support layer by any appropriate method, for example by knife coating, screen printing, roll coating or dip coating, or by other methods, but preferably by roll coating or screen printing. The porous coating preferably has a thickness of at least 30 micrometres but preferably not more than 300 and especially not more than 200 micrometres after evaporation of the solvent.

35 The assembly according to the invention may be used to provide a surface with printed information in a simple manner which may be performed entirely within the customer's plant. The assembly which will usually have a thickness in the range of from 0.1 to 1.5 mm is passed through a printer by means of which appropriate indicia are printed on the side of the assembly that has the porous coating. The printer may be a non-impact printer e.g. an ink-jet printer, or an impact printer e.g. a thermal printer, dot-matrix printer, 40 daisy wheel printer or golfball printer, and may be attached to any appropriate computer or word-processor. After the indicia have been printed on the assembly the assembly is then heated to initiate curing of the porous layer. This may be achieved by placing a number of printed assemblies in an oven or by passing the assemblies past an infrared radiation source, during which operation the porous layer will preferably be heated to a temperature of about 100°C to 200°C preferably from 150 to 170°C for up to 7 minutes. This 45 heating step causes the particles and/or fibres to melt and coalesce, and allow the components to react. Alternatively the assembly may be heated by driving it between a pair of closely spaced heated blocks. The assembly may then be attached to the surface to be marked by means of any adhesive that is provided on the opposite side of the support layer or by any other means. If the adhesive is a heat activatable adhesive, for example a hot-melt adhesive, it is possible for the uncured assembly to be positioned on the substrate 50 to be marked and heated once only to effect both the curing of the porous layer and bonding of the assembly to the substrate.

According to another preferred embodiment of the marker assembly, the support layer may be in the form of a sleeve, preferably an open-ended sleeve, so that it can be slipped over the end of a wire, cable or other item of electrical equipment. In the case of assemblies having a support layer in the form of a sleeve, it is preferred for the support layer to be dimensionally recoverable and especially for it to be 55 dimensionally heat-recoverable.

Heat-recoverable articles are articles, the dimensional configuration of which may be made substantially to change when subjected to heat treatment.

Usually these articles recover, on heating, towards an original shape from which they have previously been deformed but the term "heat-recoverable", as used herein, also includes an article which, on heating, adopts a new configuration, even if it has not been previously deformed.

5 In their most common form, such articles comprise a heat-shrinkable sleeve made from a polymeric material exhibiting the property of elastic or plastic memory as described, for example, in U.S. Patents 2,027,962; 3,086,242 and 3,597,372. As is made clear in, for example, U.S. Patent 2,027,962, the original dimensionally heat-stable form may be a transient form in a continuous process in which, for example, an extruded tube is expanded, whilst hot, to a dimensionally heat-unstable form but, in other applications, a preformed dimensionally heat stable article is deformed to a dimensionally heat unstable form in a separate
10 stage.

In the production of heat recoverable articles, the polymeric material may be cross-linked at any stage in the production of the article that will enhance the desired dimensional recoverability. One manner of producing a heat-recoverable article comprises shaping the polymeric material into the desired heat-stable form, subsequently cross-linking the polymeric material, heating the article to a temperature above the
15 crystalline point or, for amorphous materials the softening point, as the case may be, of the polymer, deforming the article and cooling the article whilst in the deformed state so that the deformed state of the article is heat-unstable, application of heat will cause the article to assume its original heat-stable shape.

The sleeves may be positioned on a relatively rigid "comb" like structure which assists in the handling and printing of the sleeves, and removed therefrom once indicia have been formed on the sleeve. Such a structure is described for example in U.S. Patent No. 3,894,731. Alternatively the support layer may be in the form of a sheet that has been bonded to itself along a series of spaced apart bond lines to define an array of marker sleeves. In yet another form, the support layer may be in the form of a continuous strip which is heat-recoverable and is supported itself on a rigid carrier strip that prevents premature recovery of the support layer when the porous coating is heated. This general type of assembly is described in British
20 Patent Specification No. 2,059,913A, the disclosure of which is incorporated herein by reference.

In these embodiments the porous layer is preferably as described above with respect to the first embodiment. In use, the sleeves may simply be separated from one another and placed on the wire or other object to be marked. The sleeve is then heated for example by means of a hot-air gun during which operation the porous coating begins to cure and render the indicia indelible and the sleeve recovers into
30 conformity with the wire or other object.

Several marker assemblies in accordance with the present invention will now be described by way of example with reference to the accompanying drawings in which:

- Figure 1 is a perspective view of a panel marker in accordance with the invention;
- Figure 2 is a section through part of the marker of figure 1 with the thickness of the layers
35 exaggerated for the sake of clarity;
- Figure 3 is a section through part of an alternative form of marker;
- Figure 4 is a perspective view of another form of assembly in accordance with the invention, and
- Figure 5 is a perspective view of yet another form of assembly.

Referring to figures 1 and 2 of the accompanying drawings, a panel marker 1 comprises a flat, flexible
40 support layer 2 formed from a polyester. On one side of the support layer 2 a powdered epoxy/polyamide curable coating 3 has been formed by a knife coating method. The coating 3 has the formulation given in Example 1 below. On the other side of the support layer 2 is a layer of polyamide hot-melt adhesive 4 and a silicone coated release paper 5. The total thickness of the assembly is about 400 micrometres.

The assembly is simply passed through a printer, for example an ink-jet printer, in order to print the
45 indicia 6 on the porous layer and the printed marker is then exposed to an infrared radiation source for a period of about 3 to 5 minutes in order to fuse the epoxy and polyamide particles and initiate curing of the porous layer. The marker is then ready to be adhered to the surface by means of the hot melt adhesive layer 4.

By appropriate choice of the particle size for the porous layer it is possible for a number of surface
50 finishes to be obtained, ranging from very smooth finishes with particles of less than 10 micrometres to coarse finishes with particles larger than 100 micrometres. Where the particles have sizes in the range of from 10 to 100 micrometres, the surface will have a matt finish and so reduce unwanted reflected light.

Figure 3 shows an alternative form of marker with the thickness of the layers also exaggerated. In this form of marker the thickness of the support has been considerably increased by means of an additional
55 layer 10 that is bonded to the support layer 2 by means of adhesive layer 11. The additional layer is formed from an aromatic polyester polymer that is highly filled with alumina trihydrate in order to flame retard the layer.

Figure 4 shows a marker assembly which comprises a "comb" support structure 21 having a spine 22 that is provided with a number of sprocket holes 23, and an array of bars 24 that extend from one side of the spine 22. Each bar 24 has a heat recoverable sleeve 25 partially recovered thereon, and the outer surface of each sleeve is provided with a curable particulate epoxy/polyamide coating.

The assembly can be fed into a conventional typewriter or printer, with suitable modification to the typewriter or printer platten, and a flat surface of each heat-shrinkable sleeve will be presented to the printer head in correct register for printing indicia on the assembly. After printing the sleeve is slipped onto a wire or other object to be marked and heated to recover the sleeve onto the substrate and to initiate curing of the coating.

Figure 5 shows another form of marker assembly that has been formed as described in British Patent Application No. 2,082,110A by stretching a pair of thermoplastic sheets 30 and 31 at a temperature below their melting or softening point, bonding the sheets together to form a plurality of open-ended sleeves 32 separated from one another by bonded portions 33 that contain lines of weakness to allow individual sleeves to be removed. After the sheets have been bonded together, the assembly is irradiated by means of high energy electrons in order to cross-link the polymeric material forming the sheets. The sheets 30 and 31 have been formed from low density polyethylene. After the sheets have been stretched, and bonded together each side of the assembly so formed is solution coated or roll coated with a particulate curable epoxy/polyamide coating as described above.

As with the other arrays, described above, the array may be passed through a conventional printer and, indicia have been formed thereon, individual sleeves may be positioned about a wire and heated to cause it to recover onto the wire and initiate curing of the epoxy/polyamide coating.

The following Examples illustrate the invention:

Example 1

A particulate epoxy composition having the composition given in Table I was formed by cryogenically grinding the epoxy resin, the polyamide, the epoxy diamine adduct and the ethylene/vinyl acetate/acrylic acid terpolymer in a Moulinex grinder blender and sieving the particles to a particle size of 53 to 99 micrometres. After grinding, all the components with the exception of the polyethylene oxide were thoroughly mixed together and were added to a 5% aqueous solution of the polyethylene oxide (310 cm³ of water) to form an aqueous dispersion.

TABLE I

	<u>Component</u>	<u>Trade Name</u>	<u>Parts by Weight</u>
5	Epoxy Resin	DER 662	100
10	Polyamide (cure agent)	Macromelt 6071 (ex Henkel)	25
15	Ethylene diamine - bisphenol A epoxy adduct (cure agent)		75
20	Aluminosilicate filler		17
25	Acid/Ethylene/vinyl acetate terpolymer (flexibilizer)	CXA 2002 (ex Du Pont)	15.5
30	Polyethylene oxide (binder)	Polyox (ex Union Carbide)	15.5
35	Zinc Oxide		5
40	Zinc Sulphide <u>or</u> Titanium Dioxide (filler)		

45 The dispersion was then coated onto a 120 micrometre thick polyester sheet using a 4 inch wide doctor blade knife coater to form a 300 to 500 micrometre thick layer. After coating the dispersion was allowed to dry at room temperature for 4 to 12 hours (although drying in air for 4 hours followed by 4 hours under vacuum is preferred).

50 The assembly so formed was printed with characters in a variety of colours using a Tektronix (trade name) 4695 ink jet printer. The assembly was then heated to about 100 to 200°C for 3 to 5 minutes using an infrared source in order to cure the coating and render the characters indelible.

55 The cured assemblies had a matt surface finish and displayed the printed indicia clearly with no loss of definition or colour. The assemblies were tested for solvent resistance by immersing them in the solvents listed in Table II at the temperatures shown for one minute and then hand brushing them with ten strokes, this procedure being repeated a further two times. No deterioration of the assembly was detected in any solvent.

TABLE II

	<u>Solvent</u>	<u>Temperature (°C)</u>
5	isopropanol (33%)	25
10	white spirit (67%)	
	1,1,1-trichloroethane	25
15	trichlorotrifluoroethane (50.5%)	25
	dichloromethane (49.5%)	
20	deionized water	70
	methyl ethyl ketone	25
25	"Skydrol" aircraft hydraulic fluid	25

30 Example 2

A particulate epoxy composition having the composition given in Table III was formed by cryogenically grinding the epoxy resin and the epoxy diamine adduct separately to a particle size of not more than 100 micrometres and then milling the separate components in a fluid energy mill to form particles of a weight average size of 10 micrometres with substantially no particles greater than 20 micrometres. After milling all the components were thoroughly mixed together and were added to a 3% aqueous solution of polyethylene oxide to form a dispersion that contained 6.5% by weight of polyethylene oxide binder based on the solids content of the dispersion. The dispersion was thoroughly mixed using a planetary mixer followed by ball milling or high shear mixing in order to remove any agglomerates. The emulsion so formed was degassed under vacuum either during or after mixing.

After formation of the emulsion it was coated onto a 23 micrometre thick polyester film having a metallised rear surface and also onto a 50 micrometre thick white polyester film by a three roll reverse coating method conducted at a speed of 1 to 3 metres per minute. The emulsion was applied in each case to a wet thickness of from 150 to 300 micrometres, corresponding to a dry thickness of from 50 to 100 micrometres, and was dried in an oven under forced air at 70 to 80 °C for 1½ to 4 minutes.

The sheet assemblies so formed were then die cut to appropriate label sizes and could then be printed on using a standard single or multiple colour ink-jet or dot matrix printer. After printing, the assemblies could be cured in an oven at 150 to 170 °C for 3 to 5 minutes.

The cured assemblies had a smooth matt surface which displayed the indicia with sufficient definition that individual dots of an ink jet printer could be resolved, and with an accurate reproduction of the original colour. In addition, the assemblies were highly flexible and were resistant to abrasion. The assemblies were tested for solvent resistance as in Example 1 without observing any deterioration of the assemblies in any solvent.

TABLE III

<u>Component</u>	<u>Parts by Weight</u>
bisphenol A epoxy resin	100.0
ethylene diamine-bisphenol A epoxy adduct (cure agent)	61.5
Aluminosilicate filler	13.0
polyethylene oxide (binder)	12.3
Titanium dioxide (pigment)	3.8

Example 3

A marker was formed having a surface coating formed from the composition shown in Table IV.

TABLE IV

<u>Component</u>	<u>Parts by Weight</u>
bisphenol A epoxy resin	100
ethylene diamine-bisphenol A epoxy adduct (cure agent)	30
Titanium dioxide (pigment)	54.5
Antioxidant	1.3
UV stabiliser	5.2
Polyethylene oxide (binder)	13.3

The epoxy component and the ethylene-diamine adduct were ground to a particle size of less than 100 μ . They were then each fluid energy milled to a mean particle size of 20 μ with none greater than 60 μ . All

components except the polyethylene oxide were then mixed and blended into a 3% solution of polyethylene oxide to form a dispersion that contained 6.5% by weight of polyethylene oxide binder based on the solids content of the dispersion. The dispersion was then coated onto 120 μ thick polyester sheet using a 4 inch wide doctor blade knife coater to form 300-500 μ thick layer. After coating the dispersion was allowed to dry at room temperature for 4-12 hours.

The assembly so formed was printed with an IBM ink jet printer. The assembly was then heated to 160°C for 5 minutes using a convection oven in order to cure the coating and render the characters indelible.

The coating finish was matt and was tested for solvent resistance as Example 1. No deterioration was detected in any solvent.

Example 4

Example 3 was repeated with the exception that the coating had the composition shown in Table V and that the modified dicyandiamide curing agent was not fluid energy milled.

TABLE V

<u>Component</u>	<u>Parts by Weight</u>
bisphenol A epoxy resin	100
modified dicyandiamide curing agent	5.3
Titanium dioxide	12.6
Aluminosilicate filler	5.3
Polyethylene oxide (binder)	8.4

After curing the marker exhibited a gloss finish. The assembly was tested for solvent resistance as in Example 1 without observing any deterioration of the assemblies in any solvent.

Example 5

Example 3 was repeated with the exception that the coating had the composition shown in Table VI and that, after comminution, the epoxy resin, cure agent and titanium dioxide were blended with a 50% solids latex of the ethylene propylene diene monomer (EPDM).

TABLE VI

	<u>Component</u>	<u>Parts by Weight</u>
5		
	bisphenol A epoxy resin	100
10	ethylene diamine-bisphenol A epoxy adduct (cure agent)	61.4
15	Titanium dioxide	61.4
	ethylene propylene diene monomer latex	360
20		

After curing the marker exhibited a matt finish. The assembly was tested for solvent resistance as in Example 1 without observing any deterioration of the assembly in distilled water, Skydrol or methyl ethyl ketone although some deterioration was observed in other solvents.

Example 6

Example 3 was repeated using the composition shown in Table VII and with the exception that the carboxyl terminated polyester and triglycidyl isocyanurate were not fluid energy milled and that the assembly was cured at 180 °C for 5 minutes.

TABLE VII

	<u>Component</u>	<u>Parts by Weight</u>
35		
40	carboxyl terminated polyester	100
	triglycidyl isocyanurate	7.4
45	Titanium dioxide	10.5
50	polyethylene oxide binder	5.7

After curing the marker exhibited a gloss finish. The assembly was tested for solvent resistance as in Example 1 without observing any deterioration of the assemblies in any solvent.

EXAMPLE 7

Example 3 was repeated using the composition shown in Table VIII with the exception that the carboxy terminated polyester was not fluid energy milled and that the assembly was cured at 180 °C for 5 minutes.

TABLE VIII

<u>Component</u>	<u>Parts by Weight</u>
carboxyl terminated polyester	100
bisphenol A epoxy resin	100
Titanium dioxide	20
cure rate accelerator (XB 3146 ex Ciba Geigy)	4
polyethylene oxide (binder)	14.4

After curing the marker exhibited a gloss finish. The assembly was tested for solvent resistance as in Example 1 without observing any deterioration of the assemblies in any solvent.

EXAMPLE 8

Example 3 was repeated using the components shown in Table IX with the exceptions that the polyester and isophorone di-isocyanate were ground rather than fluid energy milled and that the assembly was cured at 190 °C for 20 minutes.

TABLE IX

<u>Component</u>	<u>Parts by Weight</u>
hydroxyl terminated polyester	100
isophorone di-isocyanate (IPDI)	33
Titanium dioxide	14.5
polyethylene oxide (binder)	9.4

After curing the marker exhibited a gloss finish. The assembly was tested for solvent resistance as in Example 1 without observing any deterioration of the assemblies in any solvent.

When the assembly was solvent tested as described in Example 1 after having been printed on with a dot-matrix printer, no deterioration was observed with isopropanol/white spirit, deionised water and skydrol, although some loss of colour was observed with 1,1,1-trichloroethane, trichlorotrifluoroethane/dichloromethane and methyl ethyl ketone.

Claims

1. A marker assembly (1), which comprises a support layer (2) having a surface that is provided with a porous coating (3) of a latent curable material that is capable of receiving printed indicia (6) and that can be subsequently be cured to render the indicia substantially indelible, the porous coating being in particulate and/or filamentary form.
2. An assembly as claimed in claim 1, wherein the support layer is in the form of a flat sheet.
3. An assembly as claimed in claim 1 or claim 2, which is adapted to be secured to an object with the cured coating (3) exposed.
4. An assembly as claimed in claim 3, wherein the assembly includes a layer of adhesive (4) on the surface of the support layer opposite the porous coating.
5. An assembly as claimed in claim 1, wherein the support layer is in the form of an open-ended sleeve (25, 32).
6. An assembly as claimed in claim 1, wherein the support layer is in the form of a sheet (31) that has been bonded to itself or to another sheet (30) along a series of spaced apart bond lines (33) to define an array of marker sleeves (32).
7. An assembly as claimed in any one of claims 1 to 6, wherein the porous coating is in particulate form.
8. An assembly as claimed in claim 7, wherein the porous coating (3) will cure by reaction of a plurality of reactive components which exist separately from one another in the form of filaments and/or particles.
9. An assembly as claimed in any one of claims 1 to 8, wherein the porous coating (3) comprises an epoxy material.
10. An assembly as claimed in any one of claims 1 to 9, wherein the porous coating (3) comprises a material having free amine groups.
11. A method of marking an object which comprises forming indicia (6) on the surface of a support layer (2), the surface being provided with a porous coating (3) of a curable material that is in particulate and/or filamentary form, curing the porous coating by heat to render the indicia indelible, and securing the support layer to the object so that the cured coating is exposed.

Patentansprüche

1. Markieranordnung (1), die eine Trägerschicht (2) mit einer Oberfläche aufweist, die mit einer porösen Beschichtung (3) von einem latenten härtbaren Material versehen ist, das fähig ist, gedruckte Markierungszeichen (6) aufzunehmen, und das anschließend gehärtet werden kann, um die Markierungszeichen im wesentlichen dauerhaft zu machen, wobei die poröse Beschichtung in Teilchen- und/oder Fadenform vorliegt.
2. Anordnung nach Anspruch 1, wobei die Trägerschicht in Form eines flachen Flächenkörpers vorliegt.
3. Anordnung nach Anspruch 1 oder 2, die ausgebildet ist, um an einem Gegenstand befestigt zu werden, wobei die gehärtete Beschichtung (3) freiliegt.

4. Anordnung nach Anspruch 3, wobei die Anordnung eine Schicht von Klebstoff (4) auf der Oberfläche der Trägerschicht aufweist, die der porösen Beschichtung gegenüberliegt.
5. Anordnung nach Anspruch 1, wobei die Trägerschicht in Form einer offenendigen Hülse (25, 32) vorliegt.
6. Anordnung nach Anspruch 1, wobei die Trägerschicht in Form eines Flächenkörpers (31) vorliegt, der mit sich selbst oder einem weiteren Flächenkörper (30) entlang einer Reihe von beabstandeten Verklebungslinien (33) verklebt ist, um eine Anordnung von Markierungshülsen (32) zu definieren.
7. Anordnung nach einem der Ansprüche 1 bis 6, wobei die poröse Beschichtung in Teilchenform vorliegt.
8. Anordnung nach Anspruch 7, wobei die poröse Beschichtung (3) durch Umsetzung einer Vielzahl von reaktionsfähigen Komponenten härtet, die getrennt voneinander in Form von Fäden und/oder Teilchen existieren.
9. Anordnung nach einem der Ansprüche 1 bis 8, wobei die poröse Beschichtung (3) ein Epoxidmaterial aufweist.
10. Anordnung nach einem der Ansprüche 1 bis 9, wobei die poröse Beschichtung (3) ein Material aufweist, das freie Aminogruppen hat.
11. Verfahren zum Markieren eines Gegenstands, das folgende Schritte aufweist: Bilden von Markierungszeichen (6) auf der Oberfläche einer Trägerschicht (2), wobei die Oberfläche mit einer porösen Beschichtung (3) von einem härtbaren Material versehen ist, das in Teilchen- und/oder Fadenform vorliegt, Härten der porösen Beschichtung durch Wärme, um die Markierungszeichen dauerhaft zu machen, und Befestigen der Trägerschicht an dem Gegenstand, so daß die gehärtete Beschichtung freiliegt.

30 Revendications

1. Assemblage de marquage (1), qui comprend une couche de support (2) ayant une surface qui est munie d'un revêtement poreux (3) d'une matière ayant une aptitude au durcissement latent qui est capable de recevoir des signes imprimés (6) et qui peut être ensuite durcie pour rendre les signes pratiquement indélébiles, le revêtement poreux étant sous forme de particules et/ou de filaments.
2. Assemblage suivant la revendication 1, dans lequel la couche de support est sous forme d'une feuille plate.
3. Assemblage suivant la revendication 1 ou la revendication 2, qui est apte à être fixé à un objet avec le revêtement durci (3) à découvert.
4. Assemblage suivant la revendication 3, qui comprend une couche d'adhésif (4) sur la surface de la couche de support opposée au revêtement poreux.
5. Assemblage suivant la revendication 1, dans lequel la couche de support est sous forme d'un manchon à extrémités ouvertes (25, 32).
6. Assemblage suivant la revendication 1, dans lequel la couche de support est sous forme d'une feuille (31) qui a été liée à elle-même ou à une autre feuille (30) le long d'une série de lignes de liaison (33) espacées pour définir un réseau de manchons de marquage (32).
7. Assemblage suivant l'une quelconque des revendications 1 à 6, dans lequel le revêtement poreux est sous forme de particules.
8. Assemblage suivant la revendication 7, dans lequel le revêtement poreux (3) durcit par réaction de plusieurs constituants réactifs qui existent séparément les uns des autres sous forme de filaments et/ou de particules.

9. Assemblage suivant l'une quelconque des revendications 1 à 8, dans lequel le revêtement poreux (3) comprend une matière à fonction époxy.
- 5 10. Assemblage suivant l'une quelconque des revendications 1 à 9, dans lequel le revêtement poreux (3) comprend une matière ayant des groupes amine libres.
- 10 11. Procédé de marquage d'un objet, qui comprend la formation de signes (6) sur la surface d'une couche de support (2), la surface étant munie d'un revêtement poreux (3) d'une matière durcissable qui est sous forme de particules et/ou de filaments, le durcissement du revêtement poreux par chauffage pour rendre les signes indélébiles, et la fixation de la couche de support à l'objet de telle sorte que le revêtement durci soit exposé.

15

20

25

30

35

40

45

50

55

Fig. 1.

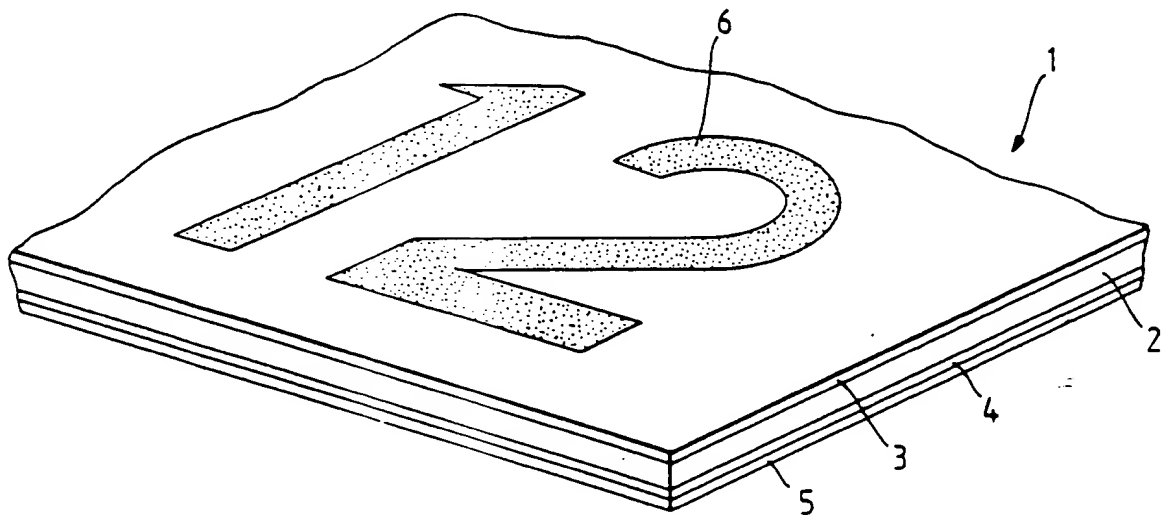


Fig. 2.

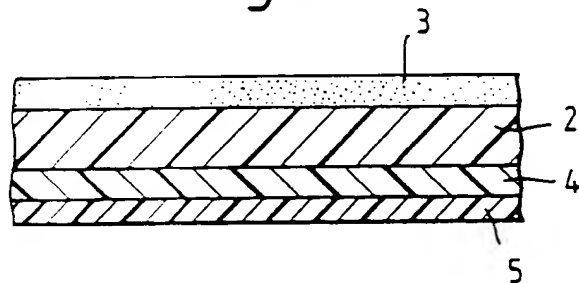


Fig. 3.

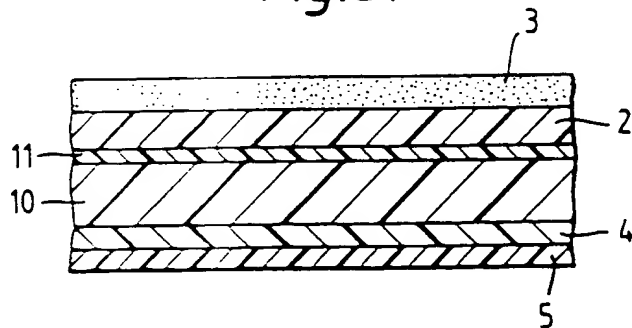


Fig. 4.

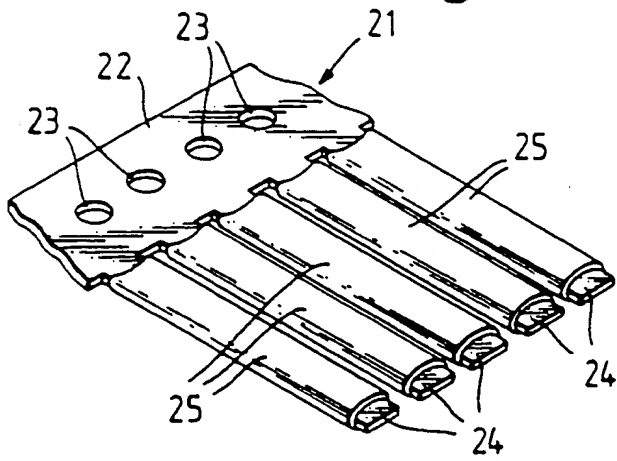


Fig. 5.

